

# A new source of ammonia and carboxylic acids in cloud water: The first evidence of photochemical process involving an iron-amino acid complex



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## ABSTRACT

In the present study we investigate the photochemical properties and impact on cloud water of ferric-aspartate complex (Fe(III)–Asp) under irradiation. Fe(III)–Asp complex was investigated as proxy of ferric-amino acids complexes that could be expected to be present in cloud water. First, the fate of complex under monochromatic (313 and 365 nm) and polychromatic ( $\lambda \geq 290$  nm) irradiation is investigated and formation quantum yields of  $\text{Fe}^{2+}$  are determined. Moreover, hydroxyl radical quantification in the presence of hydrogen peroxide is investigated at cloud water relevant concentrations and under irradiation. Obtained results suggest that hydroxyl radical formation rates are expected to be lower than those obtained considering all iron as aquacomplex or complexed with oxalate. Finally, a phototransformation mechanism for inorganic and organic products formation such as ammonia, malonic, oxalic and formic acids is proposed.

## 1. Introduction

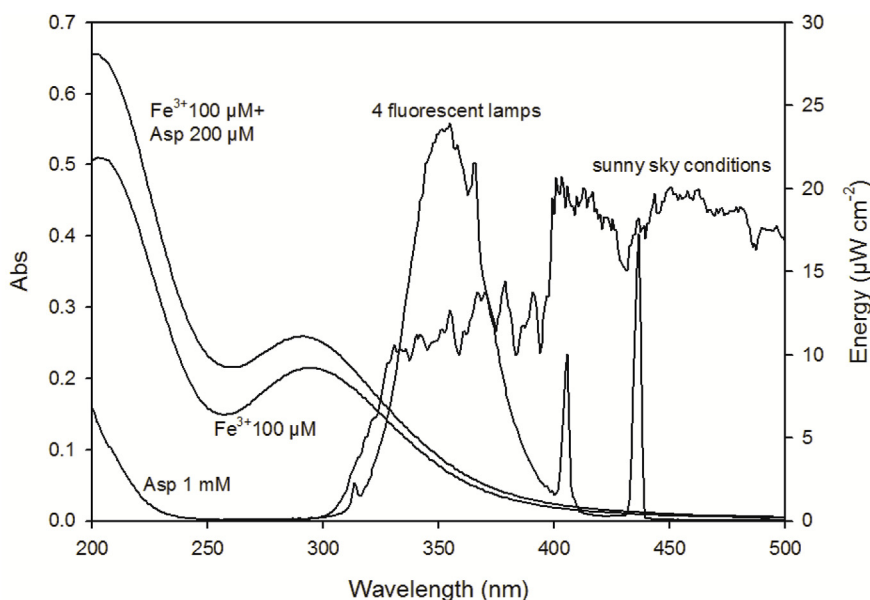
The atmosphere is a complex medium in which atmospheric particles (liquid and solid) are in continuous interaction with the gas phase. In addition to their direct effect on human health and environmental modifications, atmospheric particles are able to absorb and scatter solar radiation modifying the Earth's radiation budget (Papadimas et al., 2012; Singh et al., 2016; Zhang et al., 2017). Between the compartments of the atmosphere, cloud water droplets have attracted the attention of numerous researchers working in the field of physical-chemistry. In fact, cloud droplets can be considered as a multiphase reactor in which inorganic and organic constituents interact through numerous chemical and photochemical processes (Charbouillot et al., 2012). During the last decade, it has been clearly demonstrated that reactivity of cloud aqueous phase can impact the oxidative budget of the atmosphere. Between the oxidative species present in cloud water, hydroxyl radical ( $\text{HO}^\bullet$ ) is considered as the most important radical due to the ability to oxidize numerous organic constituents (Gligorovski et al., 2015; Herrmann, 2003; Herrmann et al., 2010). In the past few years,  $\text{HO}^\bullet$  quantification became of great interest to estimate the lifetime of organic compounds and numerous spectroscopic and chromatographic approaches have been developed. In the gas phase, the photolysis of ozone can produce electronically excited oxygen atom  $\text{O}(^1\text{D})$  which can then react with water to form hydroxyl radicals. Once in the gas phase,  $\text{HO}^\bullet$  can be transferred to aqueous phases (Henry's law

constant  $K_H = 3.0 \pm 0.2 \text{ M atm}^{-1}$ ) (Hanson et al., 1992; Mozurkewich, 1995) However, these two possible sources cannot completely explain the concentration of hydroxyl radical in cloud water (also considering the strong reactivity of this radical with organic compounds). In fact, a scarce number of studies measured the production of hydroxyl radicals in cloud water (Arakaki and Faust, 1998; Faust and Allen, 1993) and information on the oxidizing capacity of cloud water in terms of quantification of  $\text{HO}^\bullet$  and chemical sources is still a subject of debate. Between the different cloud water constituents, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), through its photolysis, is considered as one of the most important sources of  $\text{HO}^\bullet$  (Herrmann et al., 2010; Yu and Barker, 2003). Iron reactivity also contributes to the production of  $\text{HO}^\bullet$  in atmospheric aqueous phases upon Fe(III) photolysis and Fenton reaction (Deguillaume et al., 2005; Faust and Hoigné, 1990; Millero et al., 1991). However, organic constituents of cloud water such as short-chain carboxylic acids and siderophores are able to generate stable complexes with iron modifying the photoreactivity and as consequence the hydroxyl radical formation efficiency (Faust and Zepp, 1993; Long et al., 2013; Passananti et al., 2016; Weller et al., 2014). In fact, the contribution of iron species (as aquacomplexes or organic complexes) to the formation of hydroxyl radical is still a subject of debate (Bianco et al., 2015).

Recently, the presence of amino acids ranging from nM to few  $\mu\text{M}$  concentrations has been reported in cloud water collected at the top of puy de Dôme (France) (Bianco et al., 2016). Their contribution to the

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**Fig. 1.** Absorption spectra of  $\text{Fe}^{3+}$  100  $\mu\text{M}$ , aspartate 1 mM and  $\text{Fe}^{3+}$  100  $\mu\text{M}$  + Asp 200  $\mu\text{M}$  solutions at pH 3.7. Emission spectra of four fluorescent lamps reaching the solution surface and sun spectrum acquired during a spring day at Clermont-Ferrand (France).

dissolved organic matter has been estimated to be up to ~9% and, considering the high stability constant with ferric ions reported in literature, the presence of stable iron-complexes could be expected (Perrin, 1959).

In the first part of this paper, we investigate the photoreactivity of Fe(III)-aspartic acid complex as probe for iron-amino acid complexes. Aspartate diaion (Asp) was taken into account due to the presence in cloud water and the strong stability constant of complex with ferric ion ( $\log K = 11.4$ ) (Perrin, 1958). The photostability of Fe-Asp complex, considering stability constants reported in literature, is investigated using UV-vis spectroscopy under monochromatic and polychromatic irradiation. Quantum yields of ferrous ions and hydroxyl radical formation rates are determined in the presence or not of hydrogen peroxide to assess the possible impact of iron-aspartate complex photolysis on the oxidative budget of cloud water. Moreover a phototransformation mechanism leading to the formation of short-chain carboxylic acid and ammonia under polychromatic irradiation is proposed.

## 2. Material and methods

### 2.1. Chemicals

All chemicals were used without additional purification: Fe(III)-perchlorate (99.9%), aspartic acid (99.0%), malonic acid (99%), ascorbic acid (99.8%), coumarin (99%), 7-hydroxycoumarin (99%), sodium hydroxide (99.9%), perchloric acid (70%), and hydrogen peroxide were purchased from Sigma Aldrich. Ferrous perchlorate (99%), ferrozine (97%), sodium formate (99%) were purchased from Fluka. Ammonium oxalate (99%) was purchased from Prolabo. All solutions were prepared in water purified by a Millipore milli-Q device (Millipore  $\alpha\text{Q}$ , resistivity 18  $\text{M}\Omega\text{ cm}$ ,  $\text{DOC} < 0.1\text{ mg L}^{-1}$ ).

### 2.2. Complex preparation and spectroscopic characterisation

Fresh solutions of Fe-Asp complex are prepared before each experiment by mixing appropriate volumes of  $\text{Fe}(\text{ClO}_4)_3$  and aspartate stock solutions (each 10 mM). The natural pH of mixture was 3.7 and was adjusted using sodium hydroxide if necessary.

In Fig. 1 UV-vis spectrum of  $\text{Fe}^{3+}$ , Asp and Fe-Asp (100  $\mu\text{M}$  + 200  $\mu\text{M}$ ) solutions in milli-Q water at pH 3.7 are presented showing the overlap with lamp emission spectra (see irradiation

experiments description). Complex speciation is predicted using Hyperquad Simulation and Speciation (HYSS2009) software (Alderighi et al., 1999). Hydrogen peroxide was added to the solution just before each experiment in order to avoid a dark reactivity in the presence of iron (*i.e.* Fenton reaction).

### 2.3. Irradiation experiments

Photochemical experiments are performed under monochromatic and polychromatic irradiation to investigate the Fe-complex disappearance and formation of ferrous ions, hydroxyl radicals and transformation products. For monochromatic irradiation, the procedure is the following: 3 mL of solution are irradiated in a quartz cuvette (Hellma QS) under monochromatic light (313 and 365 nm) using a Hg 200 W lamp (Oriel) equipped with a monochromator. At fixed interval time the cuvette is transferred into a Varian Carry 300 UV-vis spectrophotometer to follow the time evolution of UV-vis spectra. The radiation fluxes reaching the solution at 313 and 365 nm are respectively 516 and 1230  $\mu\text{W cm}^{-2}$ . Sun-simulated irradiations are performed in homemade photochemical reactor equipped with four fluorescent lamps (Sylvania Blacklight F15W/350BL) with emission from 290 to 450 nm (centered at 350 nm).

To investigate the photochemical behavior under polychromatic radiation, 250 mL of solution are irradiated in a jacketed cylindrical reactor (length = 10 cm, volume = 30 mL) thermostated at  $283 \pm 2\text{ K}$  using a circulation cooling system under aerated conditions. The total irradiance reaching the solution in the UV region (290–400 nm) is equal to 1.27  $\text{mW cm}^{-2}$  that is closed to the value measured in a sunny day in Clermont-Ferrand (France) (1.23  $\text{mW cm}^{-2}$ ) (see Fig. 1).

The emission spectra of the irradiation systems (monochromatic and polychromatic) reaching the solution surface are recorded using an optical fiber with a charge coupled device (CCD) spectrophotometer (Ocean Optics USD, 2000 + UV-vis) which is calibrated using a DH-2000-CAL Deuterium Tungsten Halogen reference lamp.

### 2.4. Ferrous ions, hydroxyl radical formation yields and transformation products identification

Ferrous ions ( $\text{Fe}^{2+}$ ) formation is determined using ferrozine complexing agent and detection of complex is performed at 562 nm ( $\epsilon_{562\text{ nm}} = 27\,900\text{ M}^{-1}\text{ cm}^{-1}$ ) (Stookey, 1970) using a Cary 300 UV-vis

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